ESTERIFICATION OF OCTANOIC ACID AND ETHANOL USING SULFATED ZIRCONIA IN THE PRESENCE OF TRIGLYCERIDES: KINETIC AND MODELLING STUDY

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I declare that this thesis entitled *"Esterification of Octanoic acid and ethanol using sulfated zirconia in the presence of triglycerides: Kietic and Modelling Study"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Date : 28 APRIL 2009

To my beloved father and mother,
BINAR ANAK BARAYUN & EVELIN TEMAH ANAK BEGINDA

Sister and brother,
MARYLIN BINAR & BRILLIANT ELEXIUS BINAR

"*Forgive us when we fall down and lift us back up and rebuild our walls, so that the enemy is defeated in our lives"*

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ABSTRACT

The esterification of octanoic acid and ethanol using sulfated zirconia in the presence of triglycerides is one of the methods to produce biodiesel. As the fuel used today, petroleum is estimated depleted around 30-45 years in the future, Biodiesel is an alternative biofuel that can be produced using esterification method. The esterification of octanoic acid is done to determine the best operation condition to yield better conversion of octanoic acid. The operation conditions for the esterification of octanoic acid are temperature of reaction, amount of sulfated zirconia used, amount of triglycerides presence and molar ratio of octanoic acid to ethanol. The temperature of reaction ranged from 30ºC to 50ºC. The amount of sulfated zirconia used ranged from 0.5g to 1.5g. The amount of triglycerides presence ranged from 30ml to 70ml. The molar ratio of octanoic acid to ethanol ranged to 1:1 to 1:5. The best operating condition achieved for the esterification of octanoic acid and ethanol were 30ºC reaction temperature, 1.5g sulfated zirconia used, 1:1 molar ratio of octanoic acid to ethanol and 50ml of triglycerides presence in the esterification. The kinetic model been used is pseudo-homogeneous kinectic model based on the experimental data gained. The pseudo-homogeneous kinetic model gives a good agreement between the experimental data and the model used.

ABSTRAK

Esterifikasi oktanoik asid dan etanol dengan menggunakan zirkonia sulfat dalam kehadiran minyak masak merupakan satu kaedah untuk menghasilkan biodiesel. Bahan bakar yang digunakan pada maka kini, petroleum dijangka akan habis dalam masa 30-45 tahun di masa yang akan datang. Biodiesel merupakan alternatif bahan bakar bio yang boleh dihasilkan dengan menggunakan kaedah esterifikasi. Esterifikasi oktanoik asid dilakukan untuk menentukan keadaan kendalian yang terbaik untuk menghasilkan konversi oktanoik asid yang lebik baik. Keadaan kendalian untuk esterifikasi oktanoik asid adalah suhu tindak balas, jumlah zikornia sulfat yang digunakan, jumlah minyak masak yang hadir dalam esterifikasi dan nisbah molar oktanoik asid kepada etanol. Suhu tindak balas adalah dari 30ºChingga 50ºC. Jumlah zirkonia sulfat yang digunakan adalah dari 0.5g hingga 1.5g. Jumlah minyak masak yang hadir dalam esterifikasi adalah dari 30ml hingga 70ml. Nisbah molar oktanoik asid kepada etanol adalah dari 1:1 hingga &0ml. Keadan kendalian yang terbaik yang diperolehi dari esterifikasi oktanoik asik adalah pada suhu 30ºC, 1.5g zirkonia sulfat digunakan, 1:1 nisbah molar octanoik asid kepada etanol dan 50ml minyak masak digunakan untuk esterifikasi. Model kinetik yang digunakan adalah *pseudo-homogeneous* berdasarkan data experiment yang diperolehi. Model kinetik *pseudo-homogeneous* memberikan keputusan yang sejajar antara data experimen dan model itu sendiri.

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SYMBOLS	TITLE	PAGE
r	rate of reaction,	14
kc	kinetic constant,	14
ke	equilibrium constant,	14
K_M	adsorption parameter for methanol	14
K_W	adsorption parameter for water,	14
x_A	the molar fraction of the free oleic acid,	14
x_M	the molar fraction of the methanol,	14
A	preexponential factorof frequency factor	40
E	activation energy , J/mol	40
R	gas contant = 8.134 J/mol K	40
T	absolute temperature, K (Kelvin)	40

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Today's increasing price of petrol fuel make researcher to find the alternative fuel that non-petrol-based and reliable. This is because fuel used today relies in one source, petroleum. Petroleum reservoir in world is estimated depleted around 30-45 years in the future. To cope with this situation, alternative fuel that based on agricultural origin known as biodiesel are being increasingly considered as alternatives to gasoline and gas oil as sources of energy. Specifically, biodiesel has a substantial potential to reduce oil imports, dependent on petroleum and ensure continuity in the energy supply.

Biodiesel is the alternative fuel that consists of alkyl esters of long chain fatty acids. Biodiesel is made from oils or fats which are hydrocarbon. From the past, fresh soil beans oil is common used as biodiesel. Biodiesel also can be made from mustard seed oil or waste vegetables oil such as used oil from restaurant deep fryer. The advantages of using biodiesel are reducing emissions of gaseous pollutants such as carbon dioxide, can particulate matter and made from organic compounds. Biodiesel is commonly produced by transesterification of triglycerides and synthesized using alkaline catalysts. The alkaline catalysts show high performance, providing biodiesel fuel of high quality, but the oils often contain significant amounts of free fatty acids, which cannot be converted into biodiesel fuel and later then become soap.

Esterification of free fatty acids is other method in producing biodiesel that can be used as pretreatment before reaction of transesterification which convert the free fatty acids into methyl esters thus prevent saponification happens. The reaction is shown by following scheme,

R−COOH	R'−OH	R−COOR'	H_2O	
fatty acid	alcohol	biodiesel	water	(1)

Esterification of free fatty acids use catalysts to faster the reaction rate. Catalysts that commomly used in esterification is strong liquid mineral, acid catalysts. This homogenous catalyst has its side reaction that not only increasing the biodiesel production but also affect the properties of biodiesel produced.

Heterogeneous catalysts such as solid acid catalysts is the best solution due to its benefits not only on the purity of the secondary product, glycerin, but also because it will simplified downstreaming separation process, since it does not need any washing or neutralizing equipment .The heterogeneously catalyst available is resins, Cs-heteropoly acid, H zeolite and modified zirconia. The system chooses for in this esterification is octanoic acids as free fatty acids and ethanol as alcohol using sulfated zirconia as solid acids catalyst.

1.2 Problem Statement

The heterogeneously catalyzed esterification process to biodiesel production is lacking in the studies for its kinetic model and how to determine the optimum operating conditions. The importance of this data is to develop kinetic model that can represent the esterification process. Based on this problem, further research of heterogeneously catalyzed esterification based on kinetic study is done by esterification of octanioic acid and ethanol using sulfated zirconia in the presence of triglycerides.

1.3 Objective of Study

- To obtain optimum operation condition to the esterification of free fatty acid using solid acid catalyst.

- To develop a kinetic for the esterification of free fatty acid using solid acid catalyst based on the results obtains from the study.

1.4 Rational and Significance

Most of the literature review about esterification of free fatty acids is lacking about the information on its kinetic models. This model is useful reactor design. The optimum operation condition is essential in producing better quality of biodiesel.

1.5 Scope of Study

The study of esterificication of free fatty acids using solid acid catalyst will be carried out in the lab scaled batch reactor. The free fatty acids used is octanoic acid and alcohol is ethanol. Sulfated zirconia used as the solid acid catalyst. The range of study for operating; 30ºC-50ºC for temperature, 0.5g-1.5g for weight of catalyst, 30-50ml concentration of triglycerides and 1:1 -1:5 molar ratio of alcohol/free fatty acids. The kinetic model used is based on the pseudo-homogeneous kinetic model.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is non-petroleum-based diesel which consists of long-chain fatty acid methyl ethers (FAME) obtained from renewable lipids that are found in vegetable oils or animal fat. It can be used both as an alternative fuel and as an additive for commercial petroleum diesel. The advantages of using this alternative fuel other than petroleum based diesel because it is contains more than 10% oxygen, which would increase the rate of complete fuel combustion and reduce the production of pollutants. Biodiesel commonly produced by the process of transesterification of triglycerides and methanol to form methyl ester and using a homogeneous catalyst, such as sodium or potassium hydroxide dissolved in methanol. Before the transesterification took place, esterification of free fatty acids is essential to prevent free fatty acids in the base oil from coverting to soap (Saponification reaction) during the transesterification process.

2.2 Esterification

Esterification is a chemical reaction that involves two reactants, an alcohol and an acid which produce an ester as the reaction product. Esterification of free fatty acids is a fundamental step in producing biodiesel.

Caetano C.S et al., (2009) studied the esterification of fatty acids to biodiesel over polymers with sulfonic acid groups. The esterification is done using using poly(vinyl alcohol) cross-linked with sulfosuccinic acid (SSA) and polystyrene cross-linked with divinylbenzene with sulfonic acid groups, as catalysts, at 60ºC. In their findings, it was observed that the catalytic activity of poly(vinyl alcohol) (PVA) is higher than the obtained with the polystyrene (PS) ones. After about 2 h of reaction, an equilibrium conversion of 90% was achieved with PVA_SSA40 polymeric matrix. It was studied the influence of various reaction parameters, such as, molar ratio of palmitic acid to alcohol, catalyst loading and type of alcohol, on the activity of the most efficient catalyst, PVA_SSA40. In relation to the molar ratio of palmitic acid to alcohol, it was observed that when the molar ratio increases, the equilibrium conversion of palmitic acid increases from about 30% (1:3) to 90% (1:63). The esterification of palmitic acid with ethanol led to lower conversion, when compared with methanol. When the temperature was increased from 60ºC to 80ºC, an increase of the palmitic acid conversion was observed using ethanol.

Yu G.X et al., (2009) studied the esterification over rare earth oxide and alumina promoted sulfated zirconia (SZ). The esterification is done using ethanol and acetic acid. In their findings, both surface area and pore diameter of the SZ catalysts after promoted with rare earth oxide and alumina were significantly enhanced. Only tetragonal ZrO_2 (zirconia) crystal phase was formed for all the samples. In the synthesis of ethyl acetate by the esterification of ethanol and acetic acid, the catalytic activity of the SZ catalyst could not be promoted by only doping with rare earth oxides, including La_2O_3, Ce_2O_3 and Yb_2O_3. However, double promotion with Yb_2O_3 and Al_2O_3 could greatly enhance the catalytic activity and stability of the SZ catalysts. The SZAY (SO_4^{2-}/ZrO_2-Yb_2O_3-Al_2O_3) catalyst exhibited the optimal catalytic activity, reaching 86.60% at ethanol and

acetic acid molar ratio of 2:1 and 2.0 wt.%. of the catalyst, for a reaction time of 150 min under temperature of 87ºC. Their work shows that changes in catalyst activity were in close correlation with variations of the amount of moderately strong and super strong Lewis acidity. The loss of sulfur species by solvation and coking during the reaction led to the catalyst deactivation.

Ji-Yeon Park et al., (2009) studied the esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. In their findings, two heterogeneous acid catalysts Amberlyst 15 and Amberlyst BD20 were compared to determine the characteristics of a catalyst with good efficiency properties. Amberlyst BD20 showed good catalytic efficiency for high FFA oils. After reuse, the activity of Amberlyst BD20 did not decrease. An SEM micrograph revealed that the Amberlyst BD20 had no pores. Although the presence of pores in a catalyst increases the amount of active sites and thus enhances the reaction rate, a catalyst without pores is deemed to be desirable to reduce the inhibiting effect of water during the esterification of high FFA oils.

2.3 Catalyst

Catalyst is used in the estericifation process to enhance or accelerates chemical reaction process. Catalysts can be divided into two types, homogenous catalysts such as the strong liquid mineral acids, such as sulphuric acids and hydrochloric acids, heterogeneous catalyst such as solid acid catalysts with mainly Brønsted acid sites.

2.4 Homogeneous Catalyst

Aranda et al., (2007) studied acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. In their finding, small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst. The acid strength of the catalyst was responsible for the higher activity of sulfuric and methanesulfonic acids by releasing more H^+ species to protonate the carboxylic moiety of the fatty acid (rate determinant step). The higher polarity and shorter chain of methanol resulted higher activity compare to ethanol and this shows the presents steric hindrance in the reaction because higher water inhibition which attributed to phase miscibility and emulsion formation. The obtained kinetic parameters were similar to the ones reported for transesterification reaction which is indicated a similar rate determinant step because of the lower activation energy. Despite the similar protonation energy of fatty acid, Quantum chemistry studies have shown that the double bond of oleic acid increase the reactivity of carboxylic moiety of the fatty acid.

Sun R.C et al., (2000) studied fractional isolation, physico-chemical characterization and homogeneous esterification of hemicelluloses from fast-growing poplar wood. In their finding, during the alkaline treatment of the dewaxed and partially delignified fast-growing poplar wood, some alkali-labile linkages between lignin molecules, or between lignin and polysaccharides, might be broken by alkali. Acidic moieties such as carboxylic or phenolic groups, ionized in alkaline solution, might also promote the solubilization of the hemicelluloses and residual lignin, either by increasing the solubility of individual fragments or by inducing the swelling of the cell wall.

Serio D.M et al., (2005) studied synthesis of biodiesel via homogeneous Lewis acid catalyst. The homogeneous catalysts used in their synthesis were carboxylic salts (Cd, Mn, Pb, Zn). In their finding, bivalent cations are catalysts for both transesterification and esterification reactions. Catalytic activities are related to the Lewis acid strength of the metals (which must have an optimal intermediate value) and to the molecular structure of the anion. The best catalytic performances were obtained

with cation metals having a complex stability constant with dibenzoilmetane in the range between 8.60 (corresponding to cadium) and 10.23 (corresponding to zinc). Then the stearates have better performances than acetates because their higher solubility in the oil phase where the reaction occurs.

The homogeneous catalysts suffer from several drawbacks, such as the existence of side reaction with reactant, corrosive nature and the separation of catalyst from products is difficult plus environmental threats. The alternative way to overcome these drawbacks is using heterogeneous catalyst. Solid acid catalysts properties are not corrosive, can be coated onto a support and easily reused. Ion –exchange resins, zeolites, sulfated zirconia and niobium acid are the examples of catalysts used in esterification reactions.

2.5 Heterogeneous catalyst

The heterogeneous catalyst is selected due to its activity and reusability compare to conventional homogeneous catalyst. Homogeneous catalysts have side reaction with reactant and corrosive nature that can harm the environment. This weakness of homogenous catalysts leads the heterogeneous catalyst to be selected for this experiment.

The heterogeneous catalyst use in the esterification of octanoic acids and ethanol is sulfated zirconia. Sulfated zirconia is choosen as the catalyst due to its importance of its catalytic activity, reusability and thermal resistant. This modified-zirconia catalyst is thermally stable than resin-type catalyst when used at higher temperature.

Peters et al., (2005) concluded that, solid acid catalysis is very effective from the aspect of activity and reusability compared with homogeneous catalysts. The activity per proton of solid acid catalysts is significantly different due to the specific reaction rate depends on the environment of the acid sites such as hydrophobicity. The diffusion of molecules to the active sites is important in the case of porous solid acids such as